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Summary of Particle Identification Techniques

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16. ABSTRACT

In recent years there has been continuing interest in source apportionment by studying the particles collected by the sampler. These receptor methods of source apportionment are useful for control strategy development. The purpose of this document is to provide a general discussion of the methods used for particle identification, as collected by ambient samplers.

This document provides the basic information on the techniques, describes the types and properties of particles, discusses the selection of methods, provides the basic information to evaluate and apply the results of studies, and discusses the parameters to be used to select a laboratory to perform the analyses.

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VOLUME IV

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Office of Air Quality Planning and Standards
Monitoring And Data Analysis Division
Research Triangle Park, NC 27711

June 1983

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TABLE OF CONTENTS

Page

1.0 INTRODUCTION....1

2.0 PARTICLE IDENTIFICATION METHODS....2

2.1 Sampling Methods....2
2.1.1 Samplers....2
2.1.2 Filter Media....3

2.2 Analytical Methods....3
2.2.1 Optical Microscopy....3
2.2.2 Scanning Electron Microscopy....7
2.2.3 X-Ray Diffraction....9

3.0 TYPES AND PROPERTIES OF PARTICLES....11

3.1 Particle Type Terminology....11

3.2 Particle Types and Properties....14
3.2.1 Minerals....14
3.2.2 Combustion Products....14
3.2.3 Other Particles....20

3.3 Secondary Particles....20

4.0 EVALUATING AND APPLYING RESULTS....23

4.1 Sampling Devices....23
4.1.1 Sampler Location....23
4.1.2 Sampler Biases....24
4.1.3 Sampling Time....26

4.2 Filter Material....26
4.2.1 Fiber Filters....27
4.2.2 Membrane Filters....27
4.2.3 Artifact Formation....29
4.2.4 Negative Artifacts....31

4.3 Preparation of Samples....32
4.3.1 Nature of Filters....32
4.3.2 Handling of Filters and Removal of Particles From Filters....32
4.3.3 Mounting of Samples....34

TABLE OF CONTENTS (CONTINUED)

Page

4.4 Particle Size....35
4.4.2 Microscopic Size Measurement Techniques....35
4.4.2 Direct Measurement of Volume and Determination of Mass....37
4.4.3 Aerodynamic Size....38
4.4.4 Conversion of Particle Sizing Data....39
4.4.5 Errors, Biases, and Limitations....39
4.4.6 Particle Size Distributions....40
4.4.7 Creation of Size Distributions....43

4.5 Source Fingerprints....44

4.6 Quality Assurance....48

5.0 SELECTION OF METHODS....50

5.1 Methods....50
5.2 Cost of Analyses....53

6.0 SELECTION OF A LABORATORY....55

7.0 REFERENCES....57

APPENDIX....59

LIST OF TABLES

Table		Page
3.1	Common Minerals, Composition, and Possible Origins	15
4.1	Characterization of Volume (or Mass) Particle Size Distribution Modes	41
4.2	Semi-Automatic and Automatic Particle Counting and Measuring System	45
5.1	Selection of Monitors and Analysis Techniques Based on Sampling Conditions	51
5.2	Selection of Filters and Analytical Techniques	52

LIST OF FIGURES

Page

2-1 Generalized Particle Indentification System for Transparent Mineral Particles.....5

4-1 Relationships Between Particle Size Measuring Techniques.....36

4-2 Idealized Graphical Representation of a Bimodal Distribution...42

4-3 Combustion Particles and Associated X-Ray Spectra.....47

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1.0 INTRODUCTION

The purpose of this document is to provide a generalized discussion of the methods used in particle identification and characterization for source apportionment studies. This document can be used by agency personnel as a guide in commissioning source apportionment studies and interpreting the results from these studies. It is not meant to be a "how-to" manual of microscopic methods.

In the analysis of a heterogeneous mixture of particles collected on ambient filters, chemical analysis will give only the composition in terms of chemical elements or radicals. In source apportionment studies, a more detailed analysis, in which the individual particles are identified and characterized, is desirable to provide an overall picture of the origins of these particles. In many cases, particle identification provides the information necessary to evaluate the impacts of various sources on the receptors.

To accomplish the characterization and identification of individual particles, certain physical methods are used either independently or in combination with chemical analyses. This document describes these physical methods and, where appropriate, the chemical methods associated with them.

This document provides the basic information on the techniques, describes the types and properties of particles, discusses the selection of methods, provides the basic information to evaluate and apply the results of studies, and discusses the parameters to be used to select a laboratory to perform the analyses.

2.0 PARTICLE IDENTIFICATION METHODS

2.1 SAMPLING METHODS

2.1.1 Samplers

Many methods have been used for the collection of ambient particles for analysis. These include settling, impinging, and filtration. The filtration method is the only procedure discussed here since these collection devices are usually already an integral part of an agency's ambient monitoring program.

The most common ambient particulate sampler is the high volume sampler (hi-vol). The hi-vol is a simple device which draws ambient air at a rate of 1.1 to 1.7 m^3/min. (40-60 ft^3/min) through an 20-cm by 25-cm (8-in. by 10-in.) filter. The sampler is designed so that all particles smaller than about 100 μm are collected, however, collection efficiency is low for the larger particles.[1]

If only particles of a given size range are of interest, accessories are available for this purpose. The standard inlet to the hi-vol can be replaced with a cascade impactor which separates the particles according to aerodynamic diameters into several size ranges. If inhalable particulates are of concern, a size-selective inlet can be used in place of the standard inlet. This allows the collection only of those particles less than 10 μm in size.

An alternate sampling device for inhalable particulates is the dichotomous sampler. This sampler, also called a virtual impactor, fractionates and collects particle into two size ranges; coarse and fine. The coarse particles are considered to be 10 to 2.5 μm (aerodynamic) while the fine particles are less than 2.5 μm. Particles larger than 10 μm are not collected.

2.1.2 Filter Media

Several types of filter media are available for use with all of the air samplers. Each filter type has its own advantages and disadvantages depending on their intended purpose. The two major filter types are fiber and membrane. The glass-fiber filters are those normally used in ambient monitoring. These filters are not usually suitable for chemical analysis because of high background levels of impurities. Cellulose-fiber filters share the advantages of the glass fiber filters; low pressure drop and cost. They are also free of many of the impurities found in the glass fiber and are more suitable for chemical analysis. However, cellulose is a very hygroscopic material. Fiber filters are not particularily suitable for use in microscopy because particles tend to be buried in the fibers and cannot be easily seen.

Membrane filters are available in several different materials including mixed cellulose esters, polyvinyl chloride (PVC), polytetrafluoroethylene (PTFE), and silver. These filters provide fairly untextured surfaces with low particle penetration. This type of surface allows optical microscopy and SEM to be conducted easily. However, the filters do have high pressure drops, so that longer sampling times at lower flow rates are required to obtain a representative sample.

The polycarbonate filters have a nearly smooth surface. The particles collected on these filters can be easily examined through microscopy techniques and removed for elemental analysis. However, like the membrane filters, the polycarbonate filters have high pressure drops.

A more detailed discussion of filters is presented in Section 4.2.

2.2 ANALYTICAL METHODS

2.2.1 Optical Microscopy

Optical microscopy is the oldest particle identification method in use today. Despite its age, it is still a rapid, accurate technique. The information obtained by this method includes the particle structure, transparency, color, and optical properties. These characteristics can be used to identify particles.

Depending on the particle under study, reflected and/or transmitted light is used. Reflected light is used on opaque particles. Surface features, shape, color, and luster can be examined with reflected light, and in some instances, these parameters are sufficient to adequately identify the particle. Reflected light can also be used for the direct examination of particles on membrane and polycarbonate filters.

Light transmitted from below the microscope stage, passes through the particle and into the microscope tube. During the light's travel, it is subjected to various distortions and alterations by the components of the microscope and by the particle itself. One of the most important alterations to light is its polarization, i.e., the restriction of vibration to one direction. The use of polarized light is a valuable tool in particle identification.

The intent of this report is to describe the various techniques that are used to identify particles and not to present theory of operation. A generalized particle identification system for transparent particles with brief explanations of terms and techniques is presented. The system would follow that shown in Figure 2.1. The system is presented for mineral particles because of their predominance in collected particles and because most other particles would be readily identified as non-mineral. An exception to this occurs with non-spherical, non-carbonaneous combustion fly ash particles which are commonly misidentified as being minerals.

The identification system is meant to be used with a series of tables that associate the properties or parameters with lists of minerals having these properties. Reference 6 has such tables as do other texts on optical mineralogy. In many cases, a particle can be identified at a glance. In others, only a few of the grain's properties must be examined. In others, the entire system must be followed. Many of the terms presented here are defined in Section 3.1.

Color -- Color is often a key to mineral identification. In addition to color, a grain should be checked for pleochroism using polarized light. Pleochroism is the change in color exhibited by anisotropic minerals when the microscope stage is rotated. Isotropic minerals do not show pleochroism.

Habit (Shape and Form) -- Many minerals consistently assume a particular shape or form. Such a tendency is called habit.

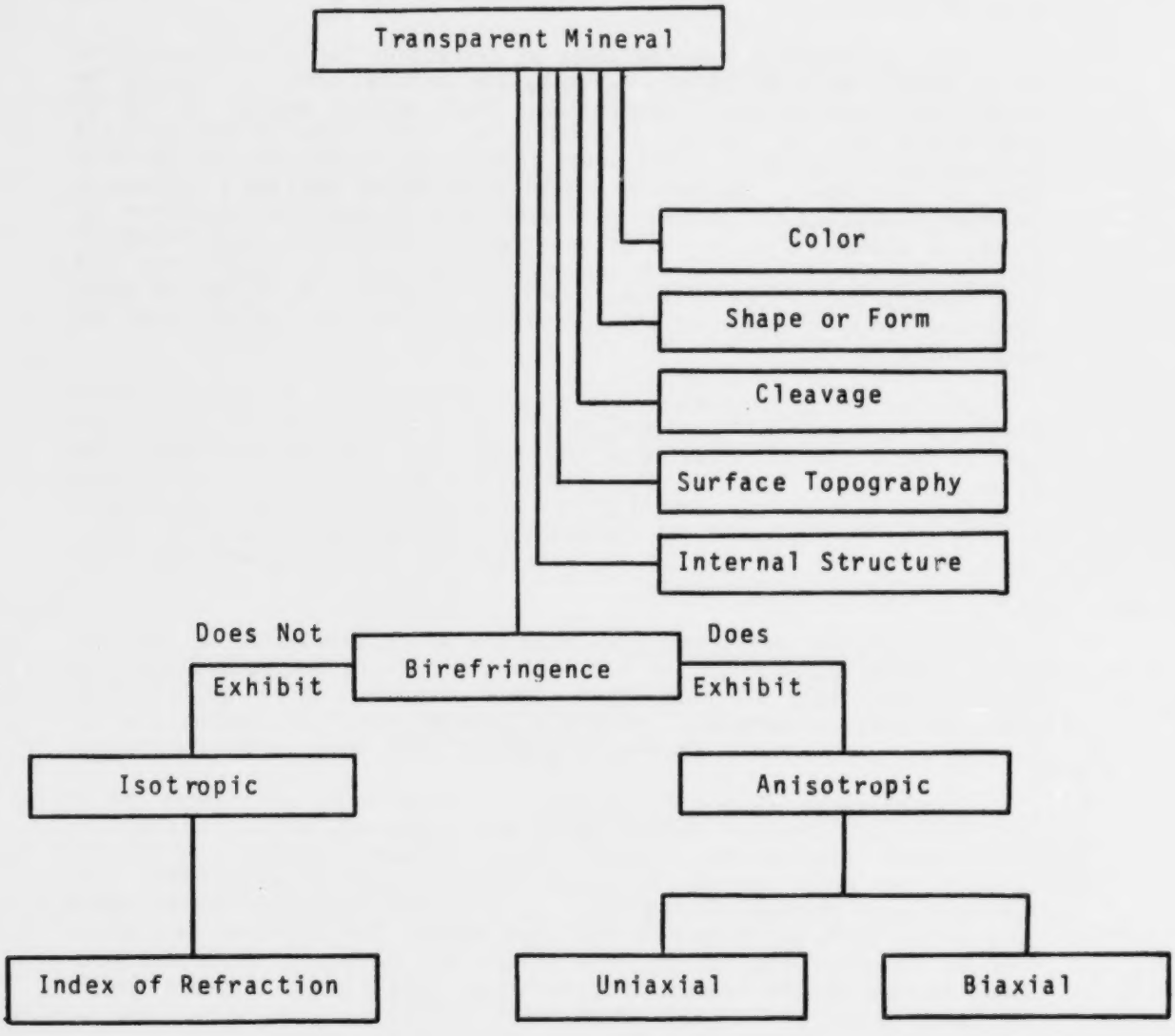

Figure 2-1. Generalized Particle Identification System for Transparent Mineral Particles

Cleavage -- Cleavage, parting, and fracture are sometimes characteristic of minerals.

Index of Refraction -- The index of refraction for mineral particles can be determined with the microscope by two methods; central illumination (Becke line) and oblique illumination. Both methods employ the use of liquids with precise indices of refraction. The index of the particle is compared to the liquid until equal indices are found, and the particle index is then known. The central illumination method employs a refraction phenomenon known as the Becke Line to measure differences in refractive indices. The Becke Line is a blur or irregular white line just inside or outside the mineral grain. As the microscope tube is raised, the line moves toward the medium of higher refractive index. A series of these tests are run with immersion oils of various refractive indices until the equal index is found.

The oblique illumination method uses a card which is inserted below the stage, and half of the light is cut off. This procedure darkens one half of the field and illuminates the other half with oblique rays. The oblique rays cause a shadow on one side of the mineral grain. If the shadow appears next to the dark side of the stage the index of the particle is less than the index of the immersion oil. When the indices are equal, the particle will be blue on one side and red on the other when white light is used for illumination.

Isotropic vs. Anisotrophic -- Minerals which crystalize in the isometric system and mineraloids are isotropic (having the same properties in all directions). In most cases, these minerals can be identified by their physical properties. Minerals crystallizing in other crystal systems are anisotropic (having properties that vary with direction).

Birefringence (Double Refraction) -- Anisotropic substances split polarized light into two vectors which have different refractive indices, which travel through the crystal along different paths of different lengths, and which vibrate in planes perpendicular to each other. The two rays pass through the analyzer (a polarizer or nicol prism) where they are aligned to vibrate in the same plane. The rays are in a position to interfere and interference colors are produced. The color produced depends on the amount of retardation (one ray is retarded due to the longer distance of travel through the grain).

The difference in the refractive indices of the two vector components is the birefringence. The maximum birefringence, or the greatest difference between the two indices of refraction, is approximately constant for a given mineral. Experienced microscopists can use the birefringence, as shown by interference colors, of a particle to assist in its identification.

Optical Character -- Anisotropic minerals are either uniaxial (having but one direction in which the light passing through the crystal is not doubly refracted) or biaxial (having two optic axes or lines of no double refraction). Interference figures are used to determine the optical character of the mineral.

Calcite and aragonite are chemically identical substances; both are $CaCO_3$. By using microscopy, these two substances may be distinguishable by noting that aragonite lacks the rhombohedral cleavage of calcite and is biaxial.

Dispersion staining is another particle identification technique that is used in optical microscopy. The sample is immersed in a liquid medium of known refractive index. The dispersion colors created by the difference between the refractive index dispersion of the sample and the immersion medium make it possible to identify particles. The procedure has been used to identify toxic dusts, minerals, and fibers. It is valid for use with both isotropic and anisotropic substances.

2.2.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) can provide information on particle size, shape, texture, and topography. Particles are examined on a one-at-a-time basis, or automated systems can be used. Elemental composition can also be determined when the appropriate analyzer is used with the microscope. In many respects SEM produces results similar to those obtained with a light microscope. It has a magnification range of 20 to 100,000 X with a depth of field which is 300 times that of the light microscope. It also has a much greater resolution ability. In the normal examination of small particles, the SEM uses magnifications of 100 to 5000 X. This provides for a resolution of 20 nm as compared to 200 nm for the light microscope.

The principle of operation of the SEM is electron optical imaging of the sample when the sample is scanned by a high energy beam of electrons. The imaging is made possible by the resulting low-energy secondary electrons and backscattered electrons. The secondary electrons emitted from the surface of the sample provide an image which appears three-demensional. During the scan, the sample can be rotated and tilted to almost any position so that all sides of the sample can be examined. This allows for the examination of irregularly shaped particles.

The usual source of the electron beam is a tungsten filament in the electron gun. Better resolution is possible by using newer filament

materials which have higher current densities and produce a smaller scanning spot. The usual diameter of the spot is about 100Å.[2] Before the electron beam reaches the sample, it must pass through a series of magnetic lenses. The final lens contains scanning coils which deflect the beam to impact the sample. The secondary electrons emitted from the sample are captured and amplified by an electron collector for display on a CRT. The magnification is controlled by the area of the sample scanned. The smaller the scan area, the greater the degree of magnification.

The sample to be scanned can be coated with a conductive material after being secured to an appropriate mount. The coating of the sample is critical for many materials since an uncoated sample can become charged and begin to deflect the electron beam. If charging occurs, very little information can be obtained from the sample's surface. The coating is applied by placing the mounted sample in a vacuum evaporator. To ensure that the coating thickness is uniform in all depressions and protrusions on the sample's surface, the sample is rotated and tilted while being coated with carbon or a metal.

The preferred conductive coatings are alloys such as gold-palladium and platinum-palladium because they provide a more uniform coat. Nonalloy metals used are aluminum and gold. The usual thickness of the coating is 5 to 10 nm. Carbon is also used as a coating material particularly where elemental composition is to be determined by X-ray analysis.

In order to provide sufficient information for accurate identification and characterization of particles, other data in addition to surface morphology are necessary. The information required is elemental composition and may be obtained by adding an energy dispersive X-ray analyzer (EDXRA) or a wavelength dispersive X-ray analyzer (WDXRA) to the SEM. The EDXRA can provide elemental composition for the elements above magnesium (Z=12), while the WDXRA is good for elements above lithium (Z=3).

The EDXRA's are photodiodes sensitive to the X-ray photons emitted from the sample's surface when exposed to the electron beam. These solid-state detectors produce electrical pulses for each photon received.

These pulses are recorded and can be displayed to provide a characterization of the X-ray wavelengths emitted by the sample. The EDXRA is a sensitive, rapid technique for determining elemental composition but is not without its limitations. The most serious problem is its inability to detect hydrogen, lithium, beryllium, boron, carbon, and nitrogen. Oxygen can only be detected with the addition of very expensive detectors. It also has fairly poor resolution for elements with adjoining X-ray lines. These problems can be overcome by applying the WDXRA to these portions of the analysis.

The WDXRA is a crystal diffraction spectrometer. By this we mean, the X-ray wavelengths from the sample are selected by each crystal in the spectrometer by diffraction. By changing the diffraction angle, all of the wavelengths can be scanned and recorded usually by a proportional counter. Although this method provides useful information, the scanning of all of the elements is time consuming. Also, the intensity of the X-rays measured is much less than the EDXRA. These shortcomings are overcome by the expanded range of elements ($Z \geq 3$) that can be analyzed.

2.2.3 X-Ray Diffraction

X-ray diffraction (XRD) is a nondestructive analytical procedure to identify and characterize individual particles or whole samples of crystalline substances. Once a compound has been identified, the results may be catalogued for future reference, an advantage as compared to other particle identification methods. Another somewhat unique ability of XRD is the identification of substances with identical chemical compositions in the solid phase. Many substances such as calcite and aragonite and quartz and cristobalite exist in chemically identical forms but are distinguishable by XRD.

XRD systems are composed of three basic components: an X-ray source, the sample, and a detection system. Depending on the application, the detector may use some type of photographic film or an electronic counter. The basic principle behind XRD is the determination of diffraction patterns of the X-rays passing through the crystal structure of the sample. This pattern is used as a measure of the interplanar spacings of the atoms in the crystal which can be used to identify the sample.

The diffraction patterns can be determined from single crystals or a powder, although fine powders are preferred. The drawback to the XRD procedure is the sample size. Good diffraction patterns are difficult to obtain with small samples. A sample size decrease is accompanied by a decrease in the number of crystals in the sample. This in turn leads to a spotty X-ray pattern. To some extent, this problem can be overcome by finely grinding the sample before analysis and increasing the detector exposure time. However, this increase in exposure time reduces the contrast between the diffraction pattern and the background, and the diffraction lines are difficult to see and measure. The decrease in contrast is caused by air-scatter of the X-rays and scatter of the X-rays caused by the sample support system. The problems can be partially overcome by removing air from the X-ray path, reducing the X-ray path length, and minimizing interference from the sample support by appropriate selection of support material and size. Many materials have been used to mount the sample including nylon, gelatin, and nitrocellulose. However, glass fibers are preferred because they are inert to solvents and allow very small particles to be easily seen.

There are many materials for which XRD is ideally suited. These include fertilizers, minerals, pigments, abrasives, corrosion products, and all other crystalline materials. The noncrystalline materials do not produce X-ray diffraction patterns and are, therefore, not suitable for analysis by this method. These include combustion glass products, biological materials, other glasses, organics, and polymers. Those materials which have large atomic numbers are much easier to analyze than light element samples because the heavier materials produce darker X-ray diffraction lines. The particle size of the sample affects the ability of XRD to provide an accurate analysis. Depending on the apparatus used, 5- μm particles can be routinely analyzed, while 1- μm particles are considered the limitation of the technique.

3.0 TYPES AND PROPERTIES OF PARTICLES

Inherent to particle source apportionment studies are characterizations of the particles collected and apportionment of the particles to various sources. In an effort to provide generalized information to the reviewer, a glossary of terms is presented, particle types are examined, and secondary particles are discussed.

3.1 PARTICLE TYPE TERMINOLOGY

Many terms are used to describe particles. Those terms referring to particle shape, size, and color are known as morphological characteristics. Other terms are used to describe surface characteristics of particles, particle inclusions and intergrowths, and, in the case of combustion products, particle encapsulation. Common terms which may be encountered in source apportionment studies are explained below.

Acicular - Needlelike: refers to the growth of a mineral in long and slender crystals.

Adamantine - Used to describe a very high luster: Metallic luster on a translucent material.

Aerodynamic diameter - The diameter of a hypothetical sphere of unit density having the same terminal settling velocity as a particle in question, regardless of its geometric size, shape, and true density.

Amorphous - Particles without apparent crystalline structure.

Angular - Having sharp edges and corners.

Bladed - Minerals strongly elongated in one direction. Expressly defined by one system as a solid in which the ratio of breadth to length is less than 2/3, and the ratio of thickness to breadth is less than 2/3.[4]

Cenosphere (Xenosphere) - Hollow spherical particles from coal and oil combustion.

Chainlike - An extended number of particles in a line.

Cleavage - The splitting, or tendency to split, along planes determined by the crystal structure. Cleavage is always parallel to a possible crystal face, that is, to a rational lattice plane of the crystal.

Columnar - Refers to the growth of crystals in column shapes.

Crystal - The regular polyhedral form, bounded by plane surfaces, which is the outward expression of a periodic or regularily repeating internal arrangement of atoms.

Dendritic - A branched pattern, like a tree or shrub.

Dull - Lacking in luster because of surface texture.

Ellipsoid - An elongated sphere.

Equant (equant grains) - Crystals or grains that have the same or nearly the same diameter in every direction.

Fibrous - A flexible particle at least 20x longer than its diameter.

Floc (flocculate) - A fine aggregation of grains or particles.

Foliated - Made up of thin leaves.

Fracture - The manner of breaking and appearance of a mineral when broken, which is distinctive for certain minerals, as conchoidal fracture.

Habit - The characteristic shape of a crystal as determined by the crystal faces developed and their shapes and relative proportions.

Inclusion - Solid, liquid or gas sealed within a particle.

Laminar - Composed of layers.

Luster - The character of light reflected by mineral surfaces. See adamantine, metallic, resinous, silky, pearly, and vitreous.

Metallic - The luster of metals.

Oölitic - A spherical to ellipsoidal body that has a concentric or radial structure or both.

Opaque - An object that does not transmit light.

Pearly - Having the luster of pearls.

Plerosphere - The encapsulated solid paticles inside of cenospheres.

Prismatic - A form of three or more similar faces parallel to a single axis.

Radiated - Applied to crystal aggregates that radiate from a center.

Relief - The appearance or visibility of outline and surface of a mineral or other particle and caused by the difference between the index of refraction of the mineral and the mounting medium. The greater the difference, the stronger is the relief.

Resinous - Resembling resin in appearance.

Rosette - A symmetrical growth form, resembling a rose. Common in gypsum, barite, and pyrite.

Rounded - Not sharp; rounded edges are common to weathered materials.

Roundness - The ratio of the average radius of the corners and edges to the radius of the maximum inscribed circle. One of the two shape measures of a particle; the other being sphericity. Roundness is a measure of the sharpness of the corners and edges of a grain.

Shard - A curved, spiculelike fragment.

Shiny - Having a surface luster.

Silky - Having the luster of silk.

Sphericity - The ratio of the normal diameter to the maximum intercept through the particle. The second of the two measures of grain shape; the other being roundness. The measure of the form of the grain independent of the sharpness of the grain edges.

Striations - A series of parallel grooves on the surface of a grain.

Tabular - A crystal flattened paralled to any face.

Translucent - Transmitting light but not capable of being seen through. Transmitting light diffusely.

Transparent - May be seen through. Transmitting light without diffusing or scattering its rays.

Undulated - Having a wavy surface.

Vesicular - Containing vesicles; small, circular, enclosed spaces.

Vitreous - Having the luster of broken glass, quartz, or calcite.

3.2 PARTICLE TYPES AND PROPERTIES

Most particle-identification, source apportionment studies divide the collected particles into four classes; minerals, combustion products, biological materials, and miscellaneous. The procedures used in this report to describe each of these classes vary due to the nature of the particle. For the minerals, possible origins of the particles are presented. For combustion products, the properties of the particles are discussed because these properties can give clues to the origin of the particles. Biological materials are not discussed because in the majority of instances, these particles are related to natural sources. Miscellaneous particles are handled similarily to the minerals.

3.2.1 Minerals

Minerals are commonly collected in airborne particulate samples. In a study of 300 filter analyses, minerals comprised an average of 65 percent (mass) of the particles on the filters.[5] Approximately 1,700 mineral species have been recognized, many of which are very rare. Some of the more common minerals which may be found on ambient filters are discussed in Table 3-1 along with their possible origins.

3.2.2 Combustion Products

Combustion products are important components of ambient particulate loading, averaging 25 percent of the filter catch.[5] Most ambient particulate studies list the following types of combustion product categories:

Combustion Products

- Soot:
  - Oil
  - Coal
  - Very fine, unidentified
- Glassy fly ash
- Incinerator fly ash
- Burned paper
- Burned wood

Oil, coal, and wood combustion products can take many forms depending on the chemical composition of the particles, the combustion zone temperature, and the particle residence time in the combustion zone. At

TABLE 3.1. COMMON MINERALS, COMPOSITION, AND POSSIBLE ORIGINS[6,7]

Minerals and Composition	Possible Origins	Comments
Elements		
Graphite, C	Mining of metamorphic rocks, notably schists; electrode & anode mfg; iron and steel	May also occur in the mining of slates, gneisses, and metamorphic limestones.
Sulphides		
Galena, PbS	Lead mining and smelting	The chief lead ore.
Sphalerite, ZnS	Zinc and lead mining and smelting	
Chalcocite, Cu_2S	Copper mining and smelting	An important copper ore
Chalcopyrite, $CuFeS_2$	Copper mining and smelting	The most important copper ore.
Pyrite, FeS_2	Metals mining and smelting, coal and slate mining	
Oxides		
Hematite, Fe_2O_3	Iron ore mining, iron and steel plants, sand	The most important iron ore. An extremely common mineral.
Ilmenite, $FeTiO_3$	Titanium ore mining, sand, iron ore mining	
Magnetite, $Fe^{II}Fe^{III}{}_2O_4$	Igneous and metamorphic rocks, sands	
Hydroxides		
Bauxite Minerals, $Al(OH)_3$ plus Al and H_2O	Aluminum smelting, bauxite mining, aluminum refining, refractories, glass	The chief ore of aluminum
Limonite, $FeO(OH)\ nH_2O$	Iron rich soils	The coloring matter of soils. An ambiguous term referring to unidentified hydrous iron oxides.

TABLE 3.1. COMMON MINERALS, COMPOSITION, AND POSSIBLE ORIGINS[6,7]

Minerals and Composition	Possible Origins	Comments
Carbonates		
Calcite, $CaCO_3$	Limestone mining, lime manufacture, cement plants, wind-blown dust	One of the most common minerals.
Dolomite, $Ca(Mg,Fe)(CO_3)_2$	Limestone and dolomite mining, lime manufacture, cement plants	
Aragonite, $CaCO_3$	Limestone and dolomite mining, cement plants, coal combustion	The calcium end of an isomorphous series of carbonates containing Ca, Ba, Sr, and Pb. Also occurs as particles on cenospheres, like gypsum.
Melilite, $Ca_2MgSi_2O_7$ or $Ca_2Al_2Si_2O_7$ or $NaCaAl\ Si_2O_7$	Mining and processing of igneous and metamorphic rocks, common in furnace slags and Portland Cement clinker slags	
Sulfates		
Gypsum, $CaSO_4 \cdot 2H_2O$	Gypsum and limestone mining, gypsum calcining, plaster making, building products, Portland cement, coal burning	Has been known to be formed in coal boiler stacks as a result of H_2SO_4 reactions with Ca in flyash. Occurs as submicron particles on cenospheres.[9]
Silicates		
Quartz, SiO_2	Sand, glass manufacture, mining operations, minerals processing, wind-blown dust, etc.	The most common of all minerals.

TABLE 3.1. COMMON MINERALS, COMPOSITION, AND POSSIBLE ORIGINS[6,7]

Minerals and Composition	Possible Origins	Comments
Silicates (con't.)		
Feldspars - K, Na, & Ca Aluminum silicates	Feldspar mining and processing, ceramics and ceramic glazes, sands, scouring powders, building and decorative stone, crushed stone, igneous rock mining and processing, some metamorphic rock mining and processing, pottery, wind-blown dust	As a group, the feldspars are the most abundant minerals.
Hornblende, $Ca_2(Mg,Fe,Al)_5(OH)_2[(Si,Al)_4O_{11}]_2$	Sands, mining and processing of igneous and metamorphic rocks	
Olivine, $(MgFe)_2SiO_4$	Refractory manufacture, sand	
Kyanite, Al_2SiO_5	Refractory for porcelains, high-temperature bricks, and spark plugs, sand	
Beryl, $Be_3Al_2(SiO_3)_6$	Beryllium manufacture and Be ore mining, beryllium alloys	The principal beryllium ore
Muscovite (Mica), $KAl_2(OH)_2(AlSi_3O_{10})$	Mica processing, mining and procesing of metamophic and granitic rocks, sands, capacitors, tubes (electronic), gage glass and diaphrams, rubber, paint, joint cement	
Biotite (Mica), $K_2(Mg,Fe)_2(OH)_2(AlSi_3O_{10})$	Igneous or metamorphic rock mining and processing, sands	

TABLE 3.1 COMMON MINERALS, COMPOSITION, AND POSSIBLE ORIGINS[6,7]

Minerals and Composition	Possible Origins	Comments
Silicates (con't.)		
Talc, $Mg_3(OH)_2\ (Si_2O_5)_2$	Ceramics, paint, plastics, paper, cosmetics, rubber, roofing, and insecticide manufacture	
Pyrophyllite, $Al_2(OH)_2\ Si_4O_{10}$	Refractories, insecticide, ceramics, and roofing manufacture, and metamorphic rock mining and processing	
Serpentine Group, $Mg_3\ Si_2O_5\ (OH)_4$	Asbestos mining, olivine mining, intrusive rock mining	Garnierite, a nickel-rich serpentine, is an important nickel ore.
Kaolin Clays, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	Clay mining and processing, soils ceramics, fiberglass and mineral wool, paper coating and filling, adhesives, asphalt tile and linoleum	
Montmorillonite Clays, $(Mg,Ca)O \cdot Al_2O_3 \cdot 5SiO_2 \cdot nH_2O$	Clay mining and processing, soils, animal feed, foundry sand, iron ore pelletizing	Montmorillonite is the chief component of bentonite which is common in th Western U.S.

least two generalized classification schemes for coal fly ash have been reported.[8,9] The first, based on both optical and SEM studies, indicates five classes of fly ash; large irregular particles, solid spherical particles, particles, hollow spherical particles, hollow spherical particles containing a number of small solid particles encapsulated inside them, and agglomerates of many small spherical particles.[8]

The second classification scheme was based on optical microscopy and had eleven classes of particles.[9] The shapes of the particles were related to the exposure to combustion (i.e., residence time or temperature). As exposure increased, particles, including silicates, iron oxides and coal, tended to become more rounded until the spherical shapes were obtained.

The one exception to the exposure/roundness hypothesis appears to be particles described as angular, lacy, and opaque. These particles appear in the coarser fractions and are thought to be incompletely combusted carbonaceous material from internal boiler surfaces.

In many cases, the spherical particles may have particles adhering to their surfaces. These particles are crystals and may be acicular, elongate blades, or cuboid.[9] These crystals are probably formed from the reaction of sulfuric acid with the metals in the flyash. Very little information has been reported on these crystals, and they could be a method of fingerprinting sources if they are examined.

Wood and oil droplets undergo morphological changes due to exposure to combustion. Sawdust becomes brown, then charred black, then rounded with its edges white or gray, and then completely white or gray-white ash. The oil droplets begin to darken as volatiles are oxidized, then form a brown crusty surface; then become a rough, black, cenosphere-like material (petroleum coke); then a cloudy, vitreous particle; and then very small, clear to yellow particles.

The category of incinerator flyash is not easily defined. In general, one particle type can not be used to fingerprint all incinerators because an incinerator's emissions are dependent on the type and amount of the material to be incinerated.

Two approaches to classifying particles as incinerator flyash were obtained.[3,4] In the first, a two-step procedure is employed. In the qualitative (first) step, particles are classified by morphology, chemistry, and other criteria. In the quantitative (second) step, optical criteria are developed for each of the classes. Interferences are taken into account. Assembledges of particles based on the optical criteria are then related to source types. The optical criteria must be strictly followed for this procedure to work.

In the second approach, characterizations of source samples from incinerators are compared to the ambient samples. Assembledges of incinerator emission particle types are located in the ambient sample and "subtracted" out.

3.2.3 Other Particles

Other particles are commonly classified as biological material and miscellaneous. Biological material usually includes pollen, spores, paper, starch, and miscellaneous plant tissue. These are not usually indicative of sources and, therefore, are not discussed.

Miscellaneous particles, materials such as iron or steel, textile fibers and rubber particles are usually indicative of sources. Most rubber particles probably originated from the wear of tires. However, some may come from various tire making operations. Tire particles may be quite large and in some cases have been mistaken for combustion products.

3.3 SECONDARY PARTICLES

Although not specifically addressed in source apportionment studies, secondary particles are potentially important contributors to the ambient particle loading. The presence of secondary particles and their nuclei causes the multimodal particle distributions discussed in Section 4.4.6. In addition, secondary particles have been characterized in studies of coal fly-ash particles.[8,9]

Secondary particles are formed in the atmosphere as a result of chemical reactions. Important secondary particles include sulfates, nitrates, ammonia compounds, and organics. Important atmospheric gases which may react to form secondary particles include ammonia, nitric

oxide, nitrogen dioxide, nitric acid, sulfur dioxide, hydrogen sulfide, sulfuric acid, hydrogen chloride, and organics.

The formation of homogeneous secondary particles has at least two distinct phases; the gas phase and the particle phase. Often, the reaction mechanisms are highly complex and involve many procursors. In the gas phase, two or more gases react to form an intermediate vapor which nucleates small particles (10^{-3} μm). These small particles then grow by a number of mechanisms, including:[10]

1) diffusion and condensation of the intermediate vapor on the particle surface,
2) adsorption on the particle surface by some or all of the reactant gases,
3) adsorption of the reactant gases into the particle,
4) scavenging of nucleating vapor molecular by the particles, and
5) coagulation of the particles.

The particles grow (accumulate) into the size range of 0.2 to 2 μm.

Heterogeneous secondary particles occur as condensation of molecules of a supersaturated vapor onto foreign particles or ions due to gas-phase or catalytic reactions on the particle surface. They can also form on the surfaces of other particles in the exhausts of industrial processes. Studies of fly ash from coal combustion have shown the presence of acicular, elongate blades, and cuboid particles adhering to the fly-ash surfaces.[9] The particles were identified as $CaSO_4$ and resulted from the reaction of sulfuric acid with the metal oxides in the fly ash. Ammonium sulfates can also be formed through the reaction of sulfuric acid with ambient ammonia in the power plant stacks and on hi-vol filters.[9,11]

The examination of ambient filters which contain secondary particles may lead to several problems, the biggest of which is the possible misidentification or misclassification of the particles. A secondary particle can be mistaken for another particle and placed in an inappropriate category. Other problems include:

1) Artifacts may form on the front or inside the filter and then migrate to the backs of filters. The backs of the filters should be examined.

2) Organic particles (those with high vapor pressures) are volatilized by the SEM and are lost to the microscopist.

3) Many sulfates form on other particles. An EDXA analysis would show sulfur and the entire particle would be considered to be a sulfate when only the surface would be.

To summarize, the formation of secondary particles follows several routes. Secondary particles can be important contributors to the ambient particulate loading. However, they may not be "seen" by the microscopist, or if seen, they may be mistaken for other particles or placed in incorrect categories.

4.0 EVALUATING AND APPLYING RESULTS

The primary purpose of this section is to present enough general information to allow the user to evaluate and/or apply the results of source apportionment studies. Secondary purposes of this section are (1) to provide enough information to explain some of the concepts involved in performing these studies, and (2) to present biases and impacts on the results due to both inherent limitations of the techniques and improper use of the techniques. With these purposes in mind, the approaches to presenting the information vary in relation to the nature of the topic.

Topics discussed include sampling devices, filters, preparation of samples, particle size, fingerprinting, and quality assurance.

4.1 SAMPLING DEVICES

The collection of particles for analysis can be made with the hi-vol which is the standard ambient particle sampler used by control agencies. If more precise information is desired on different particle size ranges, several samplers are available from which to choose. Two of these devices were designed as modifications to the basic hi-vol sampling system. The cascade impactor is located under the roof of the hi-vol and can provide particle sizing on several size ranges. The size selective inlet replaces the hi-vol roof altogether and essentially allows only inhalable particles of 10 μm and less to enter. The virtual impactor or dichotomous sampler is an entirely independent sampling system which collects only inhalable particles ($\leq$10 μm) and separates the sample into fine (< 2.5 μm) and coarse (> 2.5 μm) fractions.

4.1.1 Sampler Location

All of the particulate samplers previously described are governed by the same set of siting criteria. These criteria ensure that the air flow around the sampler is unobstructed and that the sampler is not unduly

influenced by localized sources of particles. These siting criteria are summarized as follows:[12]

1. The sampler inlet must be located between 2 and 15 m above the ground.

2. The sampler inlet must be located more than 2 m from any supporting structure.

3. The sampler must be located more than 20 m from any trees.

4. The distance from the sampler to any obstacle must be at least twice the height of the obstacle protrusion above the sampler.

5. There must be an unobstructed airflow for 270 degrees around the sampler.

6. The sampler must not be located close to any incinerator or furnace flues.

7. Depending on the height of the sampler inlet, there are certain minimum spacing requirements from roads (see Figure 1, Appendix E of 40 CFR 58).

4.1.2 Sampler Biases

Each of the sampling devices has its own particular biases associated with the collection of particulates. These biases should be considered when designing a study or analyzing the results from a study.

One of the biases associated with all ambient samplers is the collection of particles that are not truly representative of the distribution of particles in the atmosphere. To be representative, the sampler must collect particles in a manner that does not physically or chemically alter them or bias the distribution. Most samplers are not able to do this because particles may be crushed or altered through reactions, and the particles are rarely, if ever, uniformly dispersed in the air. In addition, particles are not uniformly collected. In most cases, a biased population (e.g., respirable dust, mineral dust) is collected.

The hi-vol has different collection efficiencies depending on the size of the particle. For particles less than about 5 μm, the hi-vol sampler has nearly a 100-percent efficiency.[13] However, the collection efficiency decreases significantly as the particle size increases up to 50 or 60 m where the efficiency approaches zero. Around 30 μm is the

generallly accepted value for the 50-percent cutpoint. The collection efficiency of particles above 5 μm is significantly affected by wind speed, sampling flowrate, and the orientation of the sampler to the wind direction. The particle collection is least affected by orientation when the hi-vol's roof ridge is at a 45-degree angle to the wind direction.[13] This variability in the collection of the larger particle sizes along with the non-uniform deposition of particles in the filter makes the accurate characterization of hi-vol samples difficult.

The hi-vol also collects particles when it is not operating. In areas of high wind speeds, large particles can settle on the filters while the hi-vol is in its standby mode.

The high-volume cascade impactor shares all of the biases associated with the hi-vol, since it is basically an internal modification to that device. Additionally the cascade impactor has a problem inherent in its design as a particle sizing instrument. Because the particles are aerodynamically sized by impacting on a solid surface, particle bounce and reentrainment can occur. This trait is particularly pronounced at the higher mass loadings. Another problem with the impaction against solid surfaces is that single large particles can be broken into many smaller particles and produce a positive bias towards the smaller size range. Also, as with the hi-vol, the particle deposits are not uniform which hinders accurate sample analysis.

The other particle sizing modification available for the hi-vol is the size-selective inlet. The inlet is designed to correct the wind speed and directional orientation problems of the standard hi-vol shelter. The size selective inlet design also minimizes the particle breaking, bounce, and reentrainment problems of the cascade impactor. But, because particle impaction against a solid surface does occur, some reentrainment should be expected. The problem of nonuniform particle deposits on the filter also exists, as with the other hi-vol methods.

The virtual impactor or dichotomous sampler's design eliminates the particle breaking, bounce, and reentrainment problems since particle impaction on a solid is not a part of the sizing technique. The possibility of some fine-particle carryover into the coarse airstreams of the impactor does exist, but the mass data can be adjusted to compensate for

this. The sampler is not without some problems. Some of the inlets have been shown to be sensitive to wind speeds such that the cutpoint can vary. There are also fairly high internal wall losses because of large particle deposition on the internal surfaces. The sampler also has some sensitivity to ambient relative humidity. At very high humidity levels, the sampling flow rate is reduced sufficiently to affect the sampling effectiveness.

4.1.3 Sampling Time

The various methods of analysis have certain requirements on the amount of material on the filter necessary for accurate characterizations. Since the particle sampling devices are designed for optimum collection efficiencies at particular flow rates, the sampling time is the parameter which can be varied to provide some control over filter loading. In designing a sampling system, consideration should always be given to the type of analysis to be performed on the sample. Generally, microscopy requires the smallest sample be collected, preferably only a single layer of particles. The X-ray diffraction technique requires large samples for accurate analyses. The other methods of analysis' requirements are usually between these two, although the smaller samples will most often be sufficient.

Multiple samplers, each with a different sampling time, can be used to optimize the filter loadings. Also, samplers equipped with wind-direction activated motors can be used either to selectively sample ambient air or to measure the impact from a particular source.

4.2 FILTER MATERIAL

The filter material is extremely important to the proper collection and analysis of an ambient sample. The filter material is even more critical when the chemical composition of the sample is to be determined. If the selection of the filter material can be made in developing a study, care should be given to select a filter which is easily handled in the field and is compatible with the analytical techniques that will be used. If the analysis is conducted on filters already in use in a sampling network, some knowledge of the effects of the filter material on the analysis will be useful in interpreting the results. The following

discussion provides information on the chracteristics of the various types of filter media.

4.2.1 Fiber Filters

The glass-fiber filter is the most common in use in air pollution monitoring. This filter has many advantages when used to determine mass by gravimetric analysis. These include low pressure drop, high capacity, low cost, and ease of weighing. They also have the advantage of withstanding fairly high temperatures and of being nonhygroscopic. They typically exhibit a sampling efficiency of 99.7 percent for particles of 0.3-μm diameter. Although not directly applicable to source-receptor studies, the filters are not soluble in organic solvents so that organic material can be extracted by appropriate solvents for subsequent analysis.

The disadvantages of the glass fiber filter for particle identification outweigh its advantages for most applications. The fiber structure allows particles to penetrate deep into the filters. The fibers may hide particles from viewing by the microscopy techniques. This deep penetration also causes problems for the X-ray techniques by attenuating the characteristic X-rays from many of the light elements. The highest grade glass fiber filters have high background levels because of trace element contamination. The filters themselves are responsible for scattering large amounts of the X-rays. The high elemental background levels create an additional problem of artifact formation. This artifact formation has the potential to significantly distort the analytical results. A discussion of artifact formation is presented in Section 4.2.3. These problems make the glass fiber filters generally unsuitable for microscopic or elemental analysis.

Fiber filters are also available in cellulose. These filters can be obtained in grades which are very pure and have a low ash content. The disadvantages of these filters are that they have low collection efficiencies, they are not uniform, they exhibit high hygroscopic properties, and their fibers are birefringent.

4.2.2 Membrane Filters

From a microscopy standpoint, membrane filters are the best of the available filters. These filters are made from a variety of polymeric

materials including polyvinylchloride, mixtures of cellulose, cellulose triacetate, acrylonitrile, fluorinated polymers, polytetrafluoroethylene, and polycarbonate. The membrane filters can be classified into two main categories. These are the types in which the pores are formed during the creation of the filter sheets (e.g., Millipore®) and the types which have the pores formed after the sheets are made (e.g., Millipore®).

In general,the membrane filters are much preferred to the fiber filters. They have low uniform levels of trace element contamination and produce low X-ray scattering. The membrane filters are soluble in many organic solvents when particle extraction procedures are required. An advantage for analysis by microscopy is that the filter becomes transparent with the addition of a drop of liquid of the same refractive index as the filter.[14] The disadvantages of membrane filters include relatively high pressure drops, low capacity for filter loading, and a brittleness which makes them difficult to handle in the field.

Each of the membrane filter types has those advantages and disadvantages to different degrees. The Millipore-type filter has a low trace element background, a higher capacity for particulate loading, and a greater ease of handling. The filter allows for easy removal of particles for analysis. However the sponge-like structure of the Millipore makes the filter unsuitable for direct examination on the filter by SEM. The filters are also very sensitive to ambient moisture and can produce significantly different weights if analyzed gravimetrically.[15]

The Nuclepore® filter is the ideal filter for SEM analysis since it has a flat, featureless surface which allows direct examination on the filter surface and allows particles to be easily removed. It is also suitable for X-ray analysis, since it provides a low trace element background. The filter does have some disadvantages which could preclude its use for certain sampling situations. The flatness of the filter allows particles to easily become detached during handling. The filter structure also has a very low particle loading capacity which necessitates the use of a series of filters to collect sufficient mass for gravimetric analysis. The fragility of the Nuclepore® filter makes it difficult to handle in the field.[17] Since the unique pores of the Nuclepore® filter are produced as circular holes in the filter's surface, a cluster of

holes can deteriorate to form a single large hole. This can lead to a change in filter efficiency, sample loss, and nonuniform particle deposits.[16]

4.2.3 Artifact Formation

During and after the ambient sampling, extraneous particles (artifacts) may be formed on filters. Artifacts are formed from the reactions of gases and particles with the filter itself and/or other collected particles. The extent of artifact formation depends on the type of filter used, the presence or absence of reactant components, the relative humidity, and other factors.

Sulfates and nitrates are common artifacts. The formation of artifacts can lead to serious sampling errors. For example, sulfur dioxide reactions on glass fiber filters can cause a 30-percent error in total particulate mass.[17] Similarily, on glass fiber filters, nitrate artifact formation averaged 10 $\mu g/m^3$ compared to 8.5 $\mu g/m^3$ true particulate nitrate in one study.[18]

Three types of reactions were reported to occur which could lead to the formation of sulfate artifacts. These were reactions between 1) sulfuric acid aerosol and the filter itself, 2) gaseous ammonia and collected acidic sulfate, and 3) acidic aerosol and other collected particles.[28] Sulfuric acid and sulfur dioxide react with the components of glass fiber filters and many membrane filters. To avoid filter reactions with sulfuric acid in the sampled gas stream, polycarbonate (Nuclepore®) and PTFE (Mitex®) membrane filters should be used.[19]

Gaseous ammonia had little effect on dry acidic sulfates in one experimental situation.[19] However, with increased relative humidity, acidic sulfate particles were solvated. Various products, such as ammonium sulfate and ammonium sulfamate can be formed.[20]

The reaction of sulfate particles with other particles has been observed.[19] Experiments with sulfuric acid aerosol and halide (Cl,I) salts showed considerable loss of the volatile halogen acids and the formation of stable sulphate salts.[19]

In these same experiments, a difference was seen in the reactions on Nuclepore® and Mitex® filters. When using KCl as the halide salt, no

reaction occurred on dry Mitex® filters when exposed to sulfuric acid treatment, while a significant decline in the Cl/K ratio was observed on Nuclepore® filters.[19] With relative humidity at 76 percent, the Mitex® filter showed a 96-percent reduction in the Cl/K ratio when exposed to the sulfuric acid aerosol.

This same article proposed that a possible preliminary condition for particle/particle interactions was the inhomogeneous distribution of the particles on the filters. This type of distribution can result from both the improper design of the inlet to the filter holder which can lead to the local enrichment of large particles and from the agglomeration of particles around the pores of membrane filters.[19]

The oxidation of sulfur dioxide on carbon particles was investigated in two studies.[21,22] At low temperatures, the following observations were recorded:

1) in the presence of oxygen, SO_2 is oxidized on carbon to form SO_3 or H_2SO_4,
2) SO_3 and H_2SO_4 poison the surface active sites of the filters, because they do not desorb after their formation,
3) nitrogen dioxide is chemisorbed or decomposed to NO, and
4) at ambient temperatures, the amount of acid formed on carbon surfaces is increased with the addition of NO_2 to the SO_2.

In addition to carbon, Fe_2O_3, MnO_2 and particulate matter from Pittsburg have been shown to sorb SO_2.[23]

Active sites of certain filter types can fix gaseous nitrogen compounds, especially nitric acid, and cause the formation of artifact particulate nitrates. The chief artifact producing reaction appears to be the gas-filter interaction.[24] The discussion of nitrate artifact formation is separated into filter types.

Glass-fiber -- Glass-fiber filters display high nitrate artifact formation. In one laboratory study, clean filters were exposed to nitrogen dioxide and nitric acid mists.[18] The nitrogen dioxide caused comparatively little artifact formation on all filters. On glass fiber filters, the addition of ozone or ammonia caused small increases in artifact formation. With nitric acid, artifact formation was one to two orders of magnitude higher.

Another laboratory study examined the impact on artifact formation from the exposure of clean filters to NO_2, HNO_3, NH_3, PAN, and N_2O.[24] Glassfiber filters showed significant artifact formation when exposed to nitric acid and nitrogen dioxide at high humidity.

Quartz-Fiber -- Quartz-fiber filters show some nitrate artifact formation in field tests and upon laboratory exposure to nitric acid.[23,25] as much nitrate as quartz-fiber filters, although the collection efficiencies of the two filters are essentially equivalent.[25] In the lab tests, the quartz-fiber filter was judged to be superior to the glass-fiber, although some nitrate artifacts were formed from exposure to nitric acid.[24]

Spectrograde -- Nitric acid attacks the coatings on Spectrograde filters and forms a high level of artifact nitrate.[25]

Nylon -- High levels of nitrate artifacts were formed upon exposure to nitric acid and nitrogen dioxide at high humidities.[24]

Cellulose-Acetate -- Nitric acid caused the formation of substantial artifacts on cellulose-acetate filters.[24] However, other nitrogen gases had no effect.

Polycarbonate -- No significant nitrate artifacts were produced by exposing clean polycarbonate filters to nitrogen gases.[24]

Teflon® -- Nitrogen artifact formation is negligible on Teflon® filters when exposed to nitrogen gases.[24]

Teflon® filters have shown a condition termed "negative artifact formation." In one study as much as 90 percent of the collected nitrates were lost.[26] The study equated the loss to temperature on a directly proportional basis. The explanation of this phenomenon was that the nitrates were lost due to evaporation caused by the disequilibrium between the solid and gaseous nitrate phases.

4.2.4 Negative Artifacts

In addition to the evaporation of nitrates described above, negative artifacts can occur as a result of chemical reactions on the filter surface. One study described the reaction of sulfuric acid produced by the photochemical oxidation of sulfur dioxide with nitrates.[27] Nitric acid volatilizes, the sulfate ions react with the available cations to form salts, and the reduced nitrogen species are retained in the aerosol. A

conclusion expressed by this study was that in eastern cities where SO_2 is prevalent, nitrate levels would be depressed.[27]

4.3 PREPARATION OF SAMPLES

During the preparation of samples for microscopic analyses, many of the techniques used can lead to sample loss and/or changes in the samples which lead to biased results. These biased results can occur due to the nature of some filters, in the handling of the filters, in the removal of particles from the filters, in the preparation of the samples for analysis, and in the analysis of the samples.

4.3.1 Nature of Filters

Two conditions of filters are difficult to handle by microscopic examination. The first is the layered filter. In this instance, the filter has become covered with multiple layers of particles due to overloading or "blinding" by flat particles. This condition poses special problems because only the top layer can be examined. If this condition occurs, it should be noted in the examination, and the analyst should remember that the top layer may not be representative of the other layers.

The second condition is embedded particles. In this instance, particles have become embedded between fibers of the glass fiber filter or in the pores of other filters. Generally, these particles are difficult to examine or remove. This condition should also be noted in the report.

Both of these conditions can lead to biased results in that all the particles are not examined. In the case of layered filters, the top layer may or may not be representative of the other layers. In the case of embedded particles, those that are embedded are probably small, and an examination of the filter without the inclusion of these particles interjects a size-selective bias to the results.

4.3.2 Handling of Filters and Removal of Particles From Filters

Filters used to collect particles must be properly handled to avoid the loss of particles or the contamination of the filters. The proper handling techniques are discussed in the Quality Assurance Section.

A particle-laden filter received at the laboratory should be examined as is. If the filter is coated with multiple layers of particles or if further analysis of individual particles is necessary, particles can be removed from the filter or vice versa. The removal of particles can induce errors in the analysis due to loss of particles, changes in the physical structure of the particle by crushing or disaggregation, and biasing the particle examination due to size-selective removal.

To remove particles, from a filter, various techniques have been employed. Particles as small as 100 μm can be picked by tweezers, and those as small as 3 μm can be picked by a tungsten needle, sometimes dipped in an adhesive. For particles in the range of 2-4 μm, a thin film of collodion is dried around the particle, and then a block which encloses the particle is cut out and mounted.[2]

These particle-picking techniques are very size selective. In addition to being time consuming, the probability exists for particle loss and changes in the physical state of the particle through crushing or disaggregation. The high degree of skill necessary for the picking operations also limits the applicability of the technique.

Another method of particle removal from a filter is ultrasonic cleaning of the filter in a fluid. This technique is commonly used for removing particles from membrane filters where alcohol or toluene is the fluid. Problems with this technique may include:

1. disaggregation of agglomerated particles,
2. uncertain removal efficiency for particles,
3. size-biased removal, and
4. solubilization of some particles in the solvent.

The alternative to particle removal is filter removal. The two methods of filter removal, low-temperature ashing and solvent dissolving, also have drawbacks. The ashing can result in the contamination of the sample with nonashless filter material, the loss of sample, or the chemical alternation of the sample.

The dissolving of the filter is an appropriate method for membrane filters. A suitable solvent, such as acetone for cellulose ester filters and hydrofuran for PVC filters, can be used for particle/filter separation. This technique uses centrifugation and several solvent exchanges

for dissolving. The main drawback to this method is the possibility of particle loss or solubilization.

4.3.3 Mounting of Samples

The mounting of particles for analysis involves different techniques depending on which analysis method is being used. The mounting technique and media should be specified along with the analyses results.

For optical microscopy, glass slides and cover glasses are used as mounts. The particles, either on or off the filters, are placed in a mounting liquid (medium).

To obtain the relief (sharpness of outline due to contrast) that is necessary to adequately see the particles, the mounting medium should have a refractive index that is much different from the refractive index of the particle. Most particles have a refractive index in the range of 1.50 to 1.55.[2] The Aroclors®, with refractive indices of 1.64 to 1.67, are suitable viscous mounting media for most mineral applications. Aroclors® are restricted chemicals.

For electron microscopy, the sample must be mounted on a suitable substrate and mounting media. The substrate should be chosen to eliminate spurious X-ray readings when it is hit by backscattered electrons and X-rays. Beryllium, carbon, graphite, lithium fluoride, and cellulose sheets are suitable substrates. Glass microscope slides are not used because they may add sodium, calcium, silicon, and potassium to the X-ray spectra.[16]

The proper choice of mounting media is necessary to avoid sample loss due to charging of the particles and their subsequent ejection into the interior of the SEM. In addition, if the particle is submerged in the media, it may not be "seen."

For X-ray analysis, better results are obtained from uncoated particles. However, charging may occur, and a light carbon coating may be necessary.

For X-ray diffraction (XRD), a particle is selected and mounted on the end of a fiber. Supposedly, particles as small as 1 m can be analyzed using this method. The problems associated with the handling of

these small particles have been discussed. The XRD technique can also be used for examining a thick layer of particles "in place" on filters.

4.4 PARTICLE SIZE

The measurement of particle size is important to the characterization of ambient particulates. Particle size measurements are conducted in two ways; the physical measurement of size using the microscope, and the measurement of aerodynamic size using sampling equipment and particle counting equipment. The various sizes obtained from these methods are used to statistically characterize the particle distribution.

To examine these techniques and to present the problems associated with these measurements, this section will briefly explain the techniques used, the relationships between the techniques, the biases and errors associated with the techniques, and particle size distributions.

4.4.1 Microscopic Size Measurement Techniques

Particle sizes are commmonly reported as either linear dimensions, such as diameter, or as areas. Statistical linear measures and measures based on the projected area of the grain are the most common sizing techniques.

Four types of statistical linear measurements are currently used and are summarized below:

1. Martin's Statistical Diameter -- The Martin's diameter is the length of the line in a fixed direction which divides the projected grain area into two equal halves.

2. Feret's Statistical Diameter -- The maximum projected length of a grain calculated in a fixed direction.

3. Maximum Horizontal Intercept -- The maximum length of a line in a fixed direction limited by the contour of the grain.

4. Apparent Long Axis -- The maximum length of a grain.

The nominal diameter, the diameter of a circle of the same area as the grain, is the other method used for particle sizing. Graticules are used for measuring the areas. Equilization of the two areas is accomplished by fitting the circle to the grain.

Figure 4-1 shows the relationships between these size measuring techniques. The mean values obtained by Martin's diameter and the nominal dia-

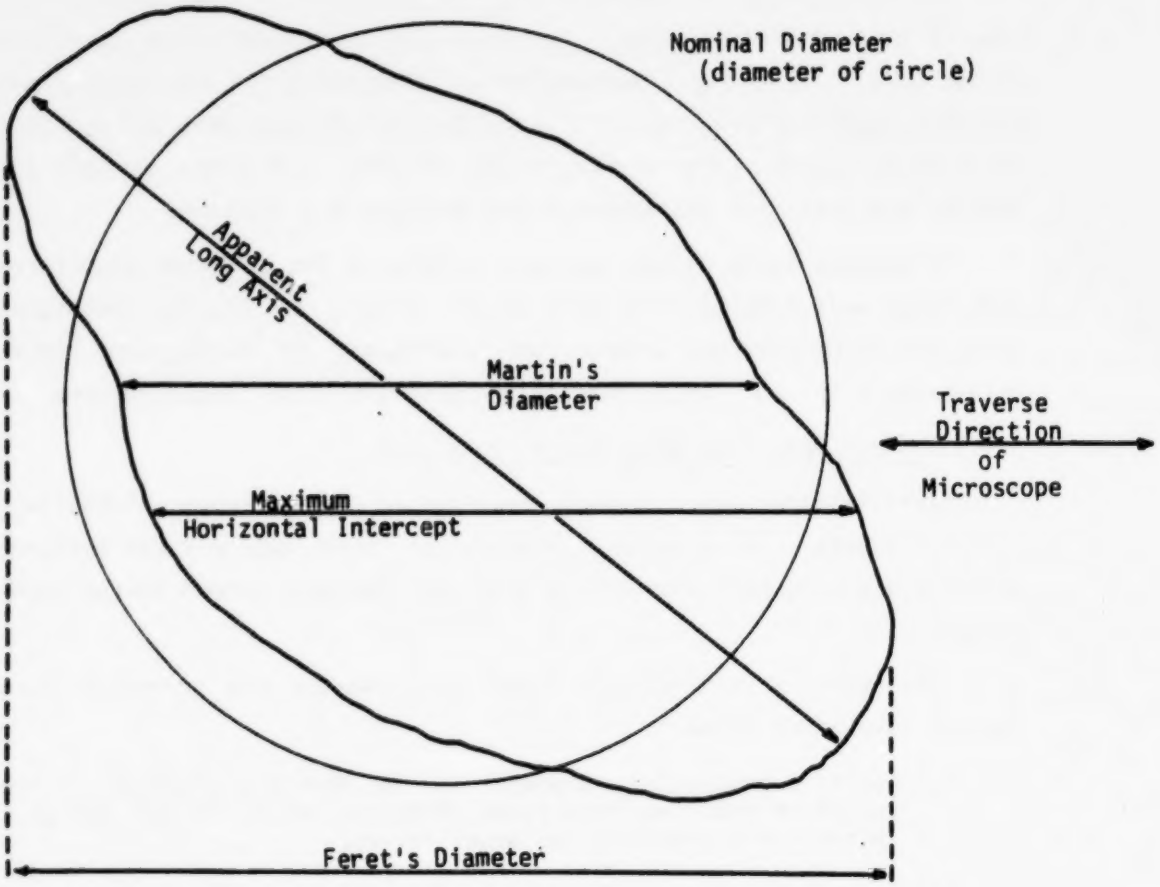

Figure 4-1. Relationships Between Particle Size Measuring Techniques

meter have been shown to agree closely with exact area measurements of "normally" shaped mineral particles.[28] For elongated particles, Martin's diameter is smaller and Feret's diameter is greater than the nominal diameter.

Since particle shape is very important to accurate particle size measurements, a description of the particle shape should be given when stating particle sizes. In addition, the method employed for measurement should also be stated.

4.4.2 Direct Measurement of Volume and Determination of Mass

The direct measurement of volume of particles is easily accomplished when the particles are perfect spheres. In the case of spheres, the volume is defined by the diameter of the sphere. As particle shape departs from that of a sphere, the volume of the particle changes in relation to the volume of a sphere of the same diameter.

As an example of this problem, the following discussion is presented.

> Assume that a cube shaped particle is oriented such that the length of one of its sides is equal to the diameter measured by Martin's method. The diameter is 1 μm. The volume of the cube-shaped particle is:
>
> $$V = a^3 = 1\ \mu m^3.$$
>
> The volume of a sphere with a diameter of 1 m is:
>
> $$V = \frac{\pi d^3}{6} = 0.5236\ \mu m^3.$$
>
> Thus, the volume of the particle as measured by Martin's diameter and assumed to be a sphere is 52.4 percent of the true volume.
>
> If the same cube-shaped particle (1 μm on side) is oriented so that the diagonal across one face is measured as the Martin's diameter, its diameter is:
>
> $$d^2 = a^2 + b^2 = 2\ \mu m^2$$
>
> $$d = \sqrt{2}\ \mu m.$$
>
> Its volume is still 1 μm^3, but the volume of a sphere of diameter $\sqrt{2}\ \mu$m is:
>
> $$V = \frac{\pi(\sqrt{2})^3}{6} = 1.481\ \mu m^3.$$
>
> Thus, the volume of the particle as measured by Martin's diameter and assumed to be a sphere is 148 percent of the true value.

As can be seen, the determination of volume for non-spherical particles can lead to large errors.

Another method that can be used to estimate the volume of particles is the measurement of vertical dimensions. This technique is applicable only to large grains that can be handled individually.

The mass of the particles can be calculated by simply multiplying the volume by the density of the particle. However, mass is not easily obtained due to the problems of measuring the volume of the particles. In addition, the density is often not known or is not correctly assumed.

4.4.3 Aerodynamic Size

In addition to the two-dimensional size measurements of particle projections, a particle can be defined by its aerodynamic size. Aerodynamic size is usually measured by the sampling device. If not measured, some sampling devices aerodynamically fractionate the particles into size cuts, e.g., the dicotomous sampler fractionates particles into two sizes, greater than 2.5 μm and less than 2.5 μ m. In some instances, particles are removed from filters, resuspended in a fluid, and settled to calculate their settling velocities.

The most commonly employed measures of aerodynamic diameter are the Stokes' diameter, the classical aerodynamic diameter, and the aerodynamic impaction diameter (also known as the Lovelace or aerodynamic resistance diameters).

The Stokes' diameter is defined by:

$$Vs = \frac{g \rho C D_s^2}{18\eta}, \quad Re \leq 0.5,$$

where: Vs = terminal settling velocity of a particle in free fall, m/sec,
g = gravitational constant (9.80665 m/sec^2),
ρ = particle density, kg/m^3,
D_s = Stokes' diameter, m,
η = fluid viscosity, kg/m-sec,
C = slip correction factor (Cunningham correction factor) for spherical particle of diameter D_s, dimensionless, and
Re = Reynold's number, dimensionless.

The classical aerodynamic diameter (D_{Ae}) is defined as:

$$D_{Ae} = \sqrt{\frac{18\eta V_s}{gC}}.$$

This diameter differs from the Stokes' diameter by assuming that the density of the sphere is unity and by calculating the slip correction factor for the classical aerodynamic diameter.

The aerodynamic impaction diameter is used for impactors and inertial classifiers and is defined as:

$$D_{Ai} = D_s\sqrt{C\,\rho}\,.$$

4.4.4 Conversion of Particle Sizing Data

Sets of particle sizing data should specify the particle sizing technique used to generate the data. In order to compare data generated by one method to data generated by another, formulas have been developed for the data conversion.

To convert particle physical diameter obtained by microscopy to aerodynamic diameter, the most commonly used method is:[9]

$$d_a = d\sqrt{\frac{\rho C}{C_a}}$$

Where: d_a = particle aerodynamic diameter, μm,
d = particle physical diameter, μm
ρ = particle density
C = Cunningham Correction Factor = 1 + 0.000621 T/d
T = temperature, °K, and
C_a = Cunningham correction for d_a.

In practice $C \approx C_a$, therefore,

$$d_a \approx d\sqrt{\rho}\,.$$

To compare the various aerodynamic diameters to each other, Reference 29 should be consulted.

4.4.5 Errors, Biases, and Limitations

The measurement of particle size with microscopic techniques can easily introduce errors, and the precision is limited by various parameters. To begin with, the "true" size of particles is difficult to determine in terms of the three-dimensional form of the particle. Therefore, particle size is based on either linear or area measurements of the two-dimensional projection of the particle, and the third dimension is ignored.

This projection leads to two problems. The first is the stability of the resting position of the particle. In general, particles mounted in low viscosity media will probably settle into their position of maximum stability. However, this may not be the case in viscous media.[28]

The second problem results from the orientation of the particle with respect to the direction of measurement. The diameter of the particle, using Martin's, Feret's, or the maximum horizontal intercept methods, is measured in a fixed direction, usually the traverse of the microscope stage. The solution to this problem is not simple. Since the microscope traverse can easily be changed by rotating the stage, many microscopists set the traverse to either the long or short axis of most of the grains. No matter what method is used, some measure or description of randomness or orientation of the particles should be given.

Other limiting parameters include:

1) Nominal diameter, measured by comparison to circles, is based on an eye-fit of the circle to the particle. This procedure requires a high degree of skill.

2) The practical limitation of the optical microscope for the sizing of particles is approximately 0.8 μm. Even with particles of the 2 or 3 μm size, errors may be high unless the microscopist is highly trained.[2]

3) Few microscope objectives have precisely marked nominal magnifications.[2] Thus, errors in size measurements are compounded by factors introduced by improper magnifications.

4) Operator fatigue has a great effect on size observations.

4.4.6 Particle Size Distributions

Suspensions of particles in the ambient atmosphere never consist of particles of homogeneous sizes. Thus, a distribution of particle sizes (i.e., the relative number of particles in each size cut) is important to study these particles. Distributions can be made of particle counts, particle mass, and particle volume. Distributions are usually described by a mean and a measure of the spread of the sizes, usually the standard deviation, in each size class.

Particle size distributions may be multimodal (with mode defined as an integral of the distribution between the minima on each side of a

maximum). In urban aerosols, there are usually one number mode, two surface modes, and two or three volume or mass modes.

The volume (or mass) distribution normally is composed of two modes; coarse and accumulation (fine). In some areas that are influenced by a source of "fresh" nuclei, a third mode, known as the Aitken mode, may occur. In these instances, the fine mode is the sum of the accumulation and Aitken modes. Characteristics of each mode are shown in Table 4.1. In general, the coarse mode is composed of primary particles that have resulted from wind entrainment of soil or dust or from other mechanical actions. The fine mode consists of secondary particles that have formed as the result of particle growth from the gas phase through condensation, combustion, or atmospheric transformation.

TABLE 4.1. CHARACTERIZATION OF VOLUME (OR MASS) PARTICLE SIZE DISTRIBUTION MODES

Mode	Size Range of Particles	Type of Particle
Coarse	$\sim$2-3 μm to $\sim$100 μm	Primary; mineral dusts, industrial particles, sea salts, etc.
Fine		Secondary (SO_4^{2-}, NO_3^-, NH_4^+, H^+, and organics) & primary combustion
Accumulation	$\sim$0.02 μm to $\sim$1-5 μm	
Aitken	$\sim$0.005 to 0.05 μm	

An idealized graphical representation of a bimodal distribution showing the coarse and fine modes is illustrated in Figure 4-2. Several features of the distribution should be explained.

1. The particle diameters at the minimum points can vary (see Table 4-1),

2. The minimum points are not zero because the size ranges overlap, i.e., some primary particles are < 1 μm in size and some secondary particles may grow to >3 μm, and

3. The magnitude of the mode integrals can vary substantially without apparent correlation to influencing factors. The primary influences are combustion sources, secondary sources, natural sources, windspeed, and atmospheric turbulence.

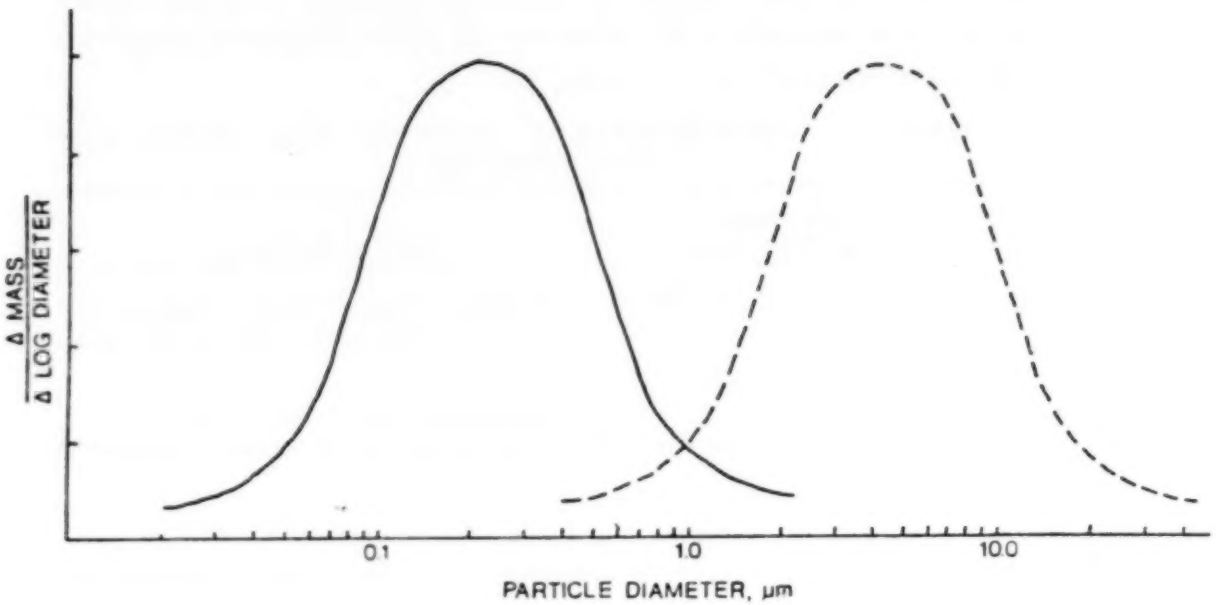

Figure 4-2. Idealized Graphical Representation of a Bimodal Distribution

The existance of multimodal particle size distributions has an impact on the collection and analysis of ambient particles. The dichotomous sampler cuts the particles at 2.5 μm. The 2.5 μm cut-size is in the minimum range between the coarse and fine modes. Therefore, the dichotomous sampler appears to be well adapted to sampling particles in two modes of urban atmospheres.

The minimum between the coarse and fine modes roughly corresponds to the lower operating range of the optical microscope. To examine the fine mode, SEM should be used.

4.4.7 Creation of Size Distributions

A size class can be any size fractinated component, such as the two cut sizes of the dichotomous samples. In some cases, the size classes can be chosen based on microscopic examination of an unfractionated sample by using ocular micrometer-scale divisions when measuring particle size.

The use of the microscope to determine size distributions of particles is difficult mainly because of the number of particles that must be counted. Sufficient particles in each size range must be counted to get significant data. The exact number of particles to be measured and counted depends on the number of size ranges and the diversity of shapes. Fairly homogeneously sized particles of nearly equal shapes may require only 100 or so particles to be counted, while highly irregularily shaped particles in many sizes may require thousands.[2]

A study discussed in Reference 28 reported that for a size range representing 20 percent by weight of the total, 400 particles within that size range should be sufficient for a 1-percent accuracy. The study also reported that to get a 0.1-percent accuracy, 40,000 particles should be counted.

The large number of particles to be counted is somewhat offset by the needed accuracy in the particle measurements. For particle distribution counts, the measurements of particle sizes do not have to be as accurate as the size measurements on single particles, because, when many particles are measured, small errors in one direction are offset and compensated for by small errors in another direction.

Another problem with microscopically measured distributions is a representative sample; the sample selected for analysis must be representative of the entire sample. To counter this problem several portions of the whole should be selected for analysis.

As shown by the above discussion, microscopic methods have limited applications when employed for the creation of particle-size distributions, especially when non-fractionated samples are being examined. For particle sizing applications, the microscope, especially the optical, should be used for the examination of relatively small numbers of particles, as a verification of aerodynamic cut-size data from samplers, and for the verification of automatic counting data.

To handle large numbers of particles, semi-automatic and automatic counting and measuring systems have been developed. Some of these devices are relatively simple, while others are complex and computer aided. A list of some commercially available instruments along with their general mode of operation is shown in Table 4-2.

4.5 SOURCE FINGERPRINTS

Particles and their characteristics can be used to trace back to their sources with varying degrees of success. These characteristics include type of particle, particle size, particle shape and freshness of cut, and particle composition. Figure 4-3 shows combustion particles and their associated X-ray spectra. The degree of success in source apportionment of particles varies on how well the particles can be characterized, on how much effort and cost are expended, and on how many sources with similar particle emissions exist in the area of impact.

In source apportionment studies, a single particle is rarely used to characterize a source. Instead, a particle assembledge is characterized by relative distributions of particle types or chemical characteristics in size ranges. These assembledges can then be compared to collected particles to reveal a relative contribution of each source.

All of these variables are related. With a variety of similar souce types, a more detailed analysis is needed, the cost increases, and certainty of results decreases. A special study can be conducted to evaluate

TABLE 4.2. Semi-Automatic and Automatic Particle Counting and Measuring Systems

Instrument and Manufacturer	General Principle of Operation
Semiautomatic Particle Sizer with Photometer Indicator Karl Zeiss, Inc.	Bright spot adjusted until operator judges that its area equals the area of a particle on a photomicrograph. The particle is then registered in the appropriate size class.
Timbrell Double Image Micrometer	The image of the particle is sheared and separated, adjusted to a fixed separation valve, and recorded in the appropriate size class.
Flying-spot Counters Various Manufacturers	A visible image (spot) is produced and superimposed on the particles. Light that is not absorbed by the particles strikes a photomultiplier tube and generates current producing an image that is recorded in the proper size class.
Quantitative Metallurgical System (QMS) Bausch and Lomb	An electro-optical system in which a scanner measures the field of view. The QMS provides automatic stage movement and control.
Quantimet Image Analyzing Computers, Ltd.	An electro-optical system.
Filar Micrometer or Screw Micrometer Malies Instrumments Ltd. and Other Manufacturers	Manual method easily adapted to semi-automatic. A scale or crosshair traverses the field of view of the microscope by using a micrometer thread. The amount of movement is indicated by the revolution of a graduated drum.
Fleming Particle Size Micrometer and Analyzer Fleming Instruments Ltd.	Similar to image shearing except a vibrating image caused by current variations is adjusted to a position of lowest shearing. The amplitude of the current at this point is proportional to the particle size.
Lark Semi-automatic Particle Counter	Measure Feret's diameter by moving particles across the field of view, and sizes are recorded by pricking holes in a paper chart.

cont'd.

TABLE 4.2. Semi-Automatic and Automatic Particle Counting and Measuring Systems (cont'd.)

Instrument and Manufacturer	General Principle of Operation
Humphries Eyepiece Micrometer	Uses two moveable hairlines attached to a cam. Electrical contacts (16 total) measure the particle.
Hornsten Instrument	A very sophisticated semi-automatic device that measures particle size, grain shape and roundness, and mineral volume frequency. A circular field of light is superimposed on the particle image. The diameter of the light field is controlled by an iris diaphragm which divides sizes into 10 classes.

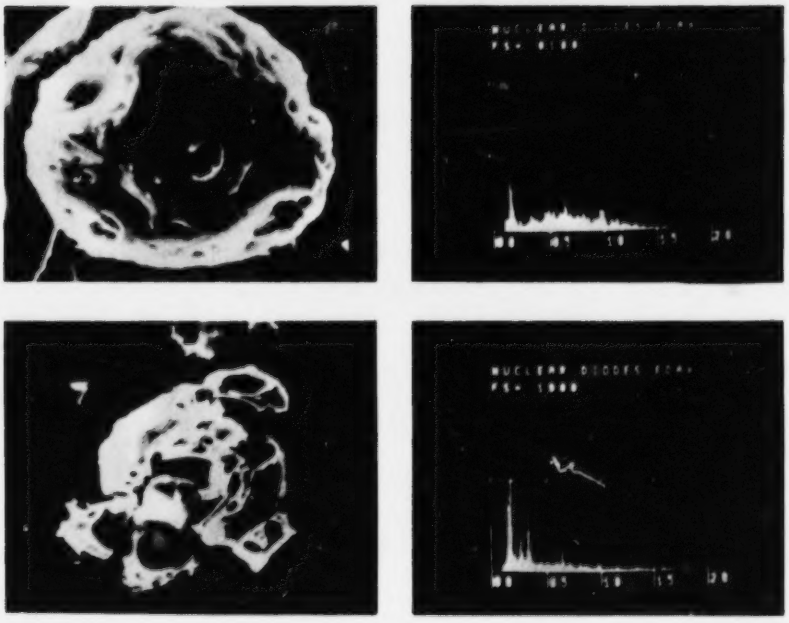

Figure 4-3. Combustion Particles and Associated X-Ray Spectra (Magnification: 1000 x ; Spectra show the presence of Al, Si, S, K, Fe, and Cu)[30]

the impact of single similar sources on ambient particle loadings. The study is designed to take advantage of special meterological conditions that segregate a particular source's emissions. These special conditions can be predicted by using dispersion modeling.

To produce source fingerprints, two major analytical techniques are used. These techniques are normally used in combination. The advantages and disadvantages of microscopy and chemical analysis as used separately and as used in combination can be stated as follows.

Methods	Advantage	Disadvantage
Microscopy	Highly accurate for identifying source types	Large errors possible in estimating relative source contribution
Chemical/Elemental Analysis	Highly accurate for chemical/elemental composition	Large errors possible in estimating relative source contribution
Combination of Microscopy & Chemical/Elemental Analysis	Highly accurate for source types and chemical/elemental composition. Agreement between the two methods is strong indication that source-type contributiion assignment is valid.	Large errors possible in estimating relative source contribution

4.6 QUALITY ASSURANCE

All aspects of source apportionment studies should be covered by quality assurance (QA) procedures. The QA procedures for ambient sampling and filter handling are discussed in Reference 12 and are not repeated here.

The QA procedures used in the particle identification and characterization aspects of the studies appear to be fairly well standardized. A good QA program should include the following procedures, at a minimum:

Optical Microscopy[3]

1. Graticule and reticule calibration,
2. Calibration of microscope objectives, and
3. Replicate analyses (usually at least 10 percent).

SEM[4]

1. Calibration of SEM magnification,
2. Replicate analyses, and
3. Calibration of X-ray spectrometer peaks.

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Table 5.1. SELECTION OF MONITORS AND ANALYSIS TECHNIQUES BASED ON SAMPLING CONDITIONS

Sampling Conditions	Type of Monitor				Analysis Technique		
	Hi-Vol	Size Selective	Cascade Impactor	Dichotomous	Optical Microscopy	SEM	X-Ray Diffraction
Budget Constraints							
Low Budget	X				X		
High Budget		X	X	X	X	X	X
Prevelent Source Type							
Industrial Process Emissions		X	X	X	X	X	X
Source of Fresh Nuclei		X	X	X		X	
Fugitive Dust		X	X	X	X		X
High Sulfate (SO_4 &/or H_2SO_4)		X	X	X	X	X	
Type of Sampling							
IP				X			
General TSP Monitoring	X						

Table 5.2. SELECTION OF FILTERS AND ANALYTICAL TECHNIQUES

Type of Monitor	Type of Filter					Analysis Techniques		
	Glass Fiber	Quartz Fiber	Cellulose Acetate	Poly-Carbonate	PTFE	Optical Microscopy	SEM	X-Ray Diffraction
High Volume	X	X				X	X	
Size-selective Inlet			X	X		X	X	X
Cascade Impactor			X	X	X	X	X	X
Dichotomous			X	X	X	X	X	X

three analysis techniques. However, fugitive dust should require only optical microscopy, unless one type of particle may require X-ray analysis for identification. The SEM could also be used for this.

In areas which are impacted by a source of fresh nuclei, such as in the vicinity of power plants, SEM is the appropriate technique because of the size range involved. In areas of high sulfate impacts, SEM is preferred but optical microscopy may be used.

The type of sampling influences the type of monitor being used. For both the IP and TSP sampling, the type of monitor is specified, and gravimetric analyses are performed.

For Table 5-2, filters and analysis techniques are compared to types of monitors. For the hi-vol, both optical and SEM are specified. The difficulties with using the techniques on fiber filters have been discussed before. When using this table, reference should be made to the sections of the report that deal with the filter media and the use of certain filters in certain types of atmospheres. For example, when sampling in high sulfate areas, PTFE filters should be used.

5.2 COST OF ANALYSES

Arriving at typical costs for the various analysis procedures is difficult because of the many different variables associated with particle identification techniques. Of prime importance to the cost level is the final use of the data received. While the costs of confirming data gathered by another technique should be relatively low, the costs for planning purposes should be higher, and those for litigation would be much higher. The use of the data dictates the precision involved and the movement from a qualitative to a semi-quantitative effort. Thus, the costs increase.

The costs to perform the two major analysis techniques are reported to be approximately $400 per filter for optical microscopy[3] and $200 to $300 per filter for scanning electron microscopy.[4] Both costs include sample preparation, sample analysis, particle sizing, and quality assurance. The SEM cost includes X-ray analysis. These costs could be typical for those associated with a planning study.

Often, both techniques are used in one study. In these cases, the costs should approach the total of $600 to $700 per filter. Somewhat

higher costs may be incurred when individual particles are "picked" from the filters for SEM analysis.

6.0 SELECTION OF A LABORATORY

The most critical decision to be made by an organization seeking assistance with particle analysis is the selection of a suitable laboratory to conduct the work. Certain parameters enter into this selection and include experience of personnel, availability of equipment, quality assurance procedures employed, backlog of work, past performance and cost.

The most important area for consideration of a laboratory to perform the work is the experience of the microscopists. Information on the background and current work areas of the microscopists at the lab should be requested. This information should include their experience with each of the specific analytical techniques.

Discussions elsewhere in this report identify the appropriate analysis methods depending on the desired results. The availability of these particular methods can be used as an initial screening criteria when evaluating several labs.

The next step in the evaluation should be much more detailed. The labs under consideration should be requested to supply a written copy of their quality assurance procedures. These can be compared to the minimum QA requirements presented in this report. Since the integrity of the sample is so important in the accuracy of the final results, the quality assurance and chain of custody procedures are one of the most important evaluation criteria.

In order for the information provided by the analysis to be useful, it must be available as soon after the sample is collected as possible. To ensure the expenditious handling of samples, the work backlog of the microscopists in the lab should be requested. This will provide some estimate of when the results of the analysis will be available.

There are two methods which can be used to judge the past performance of each lab under consideration. First, a list of former clients of each lab should be requested and several of those listed should be contacted. These clients can provide some insight as to whether the lab produced the expected results in a timely manner and in a form that was easily usable. Second, a request can also be made for the lab to supply a sample report of a study of a similar nature. The agency can then decide if the report is sufficiently detailed or requires further elaboration. Depending on the agency's capabilities, a report showing only the analysis results may be sufficient. Other agencies may want explanations and conclusions drawn from the results included in the report from the lab.

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APPENDIX

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